6.1 INTRODUCTION

Considerable research work has been done on the proton-ligand and metal-ligand stability constants in solution in last four decades. The development in this field was initiated by Jannik Bjerrum, Calvin, Bjerrum, Irving and Rossotti, Martell and Schawarzenbach have made important contributions to the rapid progress in our understanding of proton-ligand dissociation constants in aqueous as well as in mixed solvents.

Rossotti and Rossotti have defined a 'complex' as a species formed by the association of two or more simple species each capable of independent existence, when one of the simple species is a metal ion, the resulting entity is known as a metal complex. Some ligands are attached to the metal atom by more than one donor atom in such a manner so as to form a heterocyclic ring. This is known as chelation. The chelates have been extensively studied in solution as well as in the solid state by many workers because of their remarkable properties and high stability. The extensive work in co-ordination complexes have been made possible with the help of various experimental techniques and has led to a number of experimental conclusions which have been made by Martell.

The stability of a complex in solution is governed by the nature of central atom and the ligands. The most important characteristics of the central atom which influence the stability of the complex compounds are the degree of oxidation (charge on the central metal ion in case of ionic complexes), the radius and the electronic structure in case of complexes with monoatomic ligands. Stability is dependent on some characteristics in the ligand as considered for the one cation. The strength of binding for ligand
molecules and polyatomic ions depends on the nature of atoms directly linked to the central atom.

The water molecules are bound to the positive metal ion through the negative ends of the water dipoles leading to high solvation of metal ions. It is evident that a fraction of the water molecules in the environment of a metal ion directly bonded to it by the available electron pairs of the oxygen atoms of the water molecule. This fraction can be regarded as coordinated water molecules.

As expected, the number of coordinated water molecules is equal to the characteristic coordination number of ion. Because of the positive charge on metal ion, the electrons in water molecules are displaced towards the metal, which results in a loss of protons from bound water molecules. The bound molecules therefore, loses H$^+$ more rapidly than free co-solvated water molecules. A metal complex is formed by replacement of water molecules by other molecules or ions.

Frank and Wein have argued the formation of hydrogen bonded dimer of two H$_2$O molecules make it to form additional hydrogen bonds with other water molecules because of contribution (to partially co-valent hydrogen bond) of a resonance form having a partial charge separation. In other words, the formation of hydrogen bonds in the liquid is a co-operative phenomenon; that means the bonds not made and broken singly but several at a time, thus producing short lived "clusters" of highly hydrogen bonded regions surrounded by monohydrogen bonded molecules. These clusters may be expected to be compact and nearly spherical in shape. On the basis of Frank and Wein assumptions, no appreciable amount of small aggregates
Vartak and Jose\textsuperscript{5} have studied the stability constants of different sulphonic acid derivatives at 30\textdegree{}C and 0.1M ionic strength pH-metrically.

Pyrazoles, isoxazoles, thioisoxazoles, pyrazolines, isoxazolines, thioisoxazolines, carboxylic acids, dihydroxy and aminohydroxy phenols, naphthols etc. are good chelating agents due to presence of N, O, S electron donor atoms. Narwade and Jamode\textsuperscript{6} studied the formation constants and stability constants of Th(IV) complexes with some substituted pyrazolines. Khadikar et al\textsuperscript{7} have reported the metal chelates of Be(II), Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) metal ions with 3(2''-hydroxyphenyl)-5-phenyl isoxazoline. The spectral properties of 3-(2''-hydroxyphenyl)-5-phenyl isoxazoline were reported by Murthy et al\textsuperscript{8}. Pawar et al\textsuperscript{9} have studied proton-ligand and metal-ligand stability constants of transition metal ions with some substituted pyrazolines pH-metrically. Metal chelates of some substituted isoxazolines have been reported by Meshram and Narwade\textsuperscript{10}. Swalakhe et al\textsuperscript{11} have investigated proton-ligand and metal-ligand stability constants of Fe(III), Cr(III) and Al(III) metal ions with some substituted pyrazole. Ikhe and Narwade\textsuperscript{12} have studied ultrasonic velocities and adiabatic compressibility of some substituted isoxazole in 70% dioxane-water mixture at different temperatures.

The presence of donor nitrogen atom makes pyrazolines as good complexing agents. It is reported that, Cu(II), Ni(II), Mn(II), Fe(II), Zn(II), Cr(II), VO\textsubscript{2}(II), UO\textsubscript{2}(II) complexes of 4-benzoylesemicarbazone-1-phenyl-3-methyl-2-pyrazoline-5-one were prepared by Rana and Shaha\textsuperscript{13}.
The stability constants and formation constant of Th(IV) complexes with some substituted pyrazolines have been studied by Gudadhe et al. Complex of 3-(2”-hydroxyphenyl)-5-(4’-x-phenyl) pyrazoline with Cu(II) and Co(II) has been synthesised and characterised by Natrajan et al.

Proton-ligand and metal-ligand stability constants of 3,5-diaryl pyrazolines and pyrazoles pH-metrically are studied by Tayade. Coordination takes place through azomethine nitrogen of pyrazoline ring and phenolic oxygen which was revealed by IR-spectral study. Meshram et al. have studied lanthanide chelates with some substituted pyrazolines pH-metrically. Meshram et al. have also studied Eu(III) with some substituted pyrazoline complexes in different percentage of methanol-water mixture pH-metrically.

Agrawal et al. have investigated the influence of ionic strengths on stability constants of transition metal ion complexes with some substituted pyrazoles at 27°C. Thakare and Jamode have determined the stability constants of Co(II); Th(IV) metal ion complexes of substituted pyrazoles and pyrazolines. Pyrazoles are identified as good complexing agents. N-Substituted-3-methyl pyrazoles are reported with complexes of Cu(II) chloride in which coordination takes place through the donor N-atom. The complex formation between pyrazole and Ni-salts has been reported by Jansen et al.

Biological activity of substituted azopyrazoles was studied by Jolly et al. and reported by Shaha et al. for the formation of Co(II), Ni(II), Cu(II) complexes with acetone-5-methyl-pyrazole-3-carbohydrazone.

Kadu and Jamode have studied the complexes of Cu(II), Co(II) and Ni(II) with some substituted pyrazoles in 0.1 M ionic strength.
A ligand containing thiocarbamido group and coordination functions of the pyrazole ring complexes of Cu(II), Co(II), Co(III), Ni(II), Pd(II) and Zn(II) with 3,5-dimethyl-1-thiocarbamyl pyrazole is reported by Poddar et al\textsuperscript{26}. 

Sawalakhe and Narwade\textsuperscript{27} have studied role of stability constants of Cu(II) complexes with some substituted diketones at 0.1 M ionic strength by pH-metric technique. Narwade et al\textsuperscript{28} have studied the interaction between Fe(III) and Al(III) metal ions with some substituted diketones.

Lingaiah and Anadam\textsuperscript{29} have investigated the stability constants of substituted pyrazole with some bivalent transition metal ions. Meshram et al\textsuperscript{30} have investigated the metal-ligand stability constant of Eu(III), Sm(III), Tb(III), Nd(III) and Pr(III) metal ions with some substituted isoxazolines. Sawalakhe and Narwade\textsuperscript{31} have studied role of dielectric constant on proton-ligand and metal-ligand stability constants. Transition metals, lanthanides and uranyl complexes of 5-sulpho salicylic acids have been studied by Jahagirdar and Khanolkar.\textsuperscript{32}

Raghuwanshi et al\textsuperscript{33} have investigated conditional stability constants of Cu(II) complexes with some substituted chalcones and isoxazolines. Gudasi et al\textsuperscript{34} have studied synthetic characterisation and biological activity of Uranium(IV), Dioxouranium(VI) and Thorium(IV) complexes with coumarin biheterocycles. Charche et al\textsuperscript{35} studied influence of dielectric constant of dioxane-water mixture on formation constant of Cu(II) glycyI-glycyl-glycine complexes. Singh et al\textsuperscript{36} have studied the stability constants and thermodynamic parameters (\(\Delta G\), \(\Delta H\) and \(\Delta S\)) of glutathione with Cu(II), Pb(II), Ni(II), Zn(II) in aqueous medium pH-metrically at different ionic strength and temperature.
Recently, Kannappan et al\textsuperscript{37} have done ultrasonic study on dye stain removal by surfactants. Dabhi et al\textsuperscript{38} studied the formation constant of some bivalent and trivalent metal complexes with substituted pyrazolines. Acoustical study of some substituted azoles in N,N-dimethyl formamide at different temperature have been done by Gulwade et al\textsuperscript{39}. Pawar et al\textsuperscript{40} have reported studies on metal ion complexes with some substituted isoxazolines and pyrazolines pH-metrically at 1x10^{-3}M ionic strength.

The dielectric constants of substituted pyrazolines and β-diketones at 0.1 M ionic strength has been reported by Narwade and Sawalakhe\textsuperscript{41}. The complex formation of N, O and S containing heterocycles with Cu(II) metal ions was studied by Raghuwanshi et al\textsuperscript{42}. The study of effect of ionic strength on complex equilibria with peptides was made possible by Sondawale and Narwade\textsuperscript{43}. Mandakmare et al\textsuperscript{44} have investigated stability constant of Cu(II) chelates with some substituted coumarins at 0.1 M ionic strength pH-metrically. Mandakmare et al\textsuperscript{45} have also studied the formation constants of the complexes of transition metal ions with some substituted 1,3,5-triazines at different ionic strengths. Characters of Cobalt(II) complexes with some substituted pyrazoles have been studied by Gopal Narain and his coworkers\textsuperscript{46}. Sawalakhe et al\textsuperscript{47} have studied the effect of ionic strength and dielectric constants on transition metal ion complexes with some substituted sulphonic acids.

Studies on Co(II), Cu(II) and Ni(II) complexes with substituted pyrazolines and pyrazoles at 0.1 M ionic strength pH-metrically have been investigated by Khadson et al\textsuperscript{48}. Pawar and Doshi\textsuperscript{49} have reported pH-metric study on determination of proton-ligand and metal-ligand stability constants.
of some substituted isoxazolines using Calvin-Bjerrum titration technique in 70% dioxane-water mixture at 0.1M ionic strength and (30±0.1°C) temperature. Agrawal et al\textsuperscript{50} determined the metal-ligand stability constant of some substituted thiodiazoles spectrophotometrically while Raut et al\textsuperscript{51} have studied the conditional stability constants of transition metal ion complexes with captoprilt as the antibiotic drug. The interaction of Co(II) and Cu(II) metal ion complexes with some substituted isoxazolines have been studied\textsuperscript{52} using spectrophotometric technique at 0.1M ionic strength and (30±0.1°C) temperature in 70% dioxane-water mixture.

Sharma et al\textsuperscript{53} have studied thermodynamic properties of metal chelates of the La(III) ions with tridentate bıprotic ligands pH-metrically. Potdar and Rajput\textsuperscript{54} reported pH-metric study of proton-ligand and metal-ligand stability constants of Cu(II) and Fe(II) complexes with substituted pyrazoles and isoxazoles at 0.1M ionic strength. Jamode and Kale\textsuperscript{55} recently studied determination of proton-ligand stability constants (pK) and metal-ligand stability constants (logK) of Co(II), Cu(II) and Ni(II) complexes with 1-substituted pyrazoles at 0.1M ionic strength. Determination of proton-ligand and metal-ligand stability constants of transition metal complexes with pyrazole moiety have been reported by Omar\textsuperscript{56} using pH-metric technique.

**Application of Co-ordination Complex :**

Co-ordination complexes cover a wide range of applications in various fields of human interest. Some of the important applications are as follows.

1] Separation and purification of lanthanides have been studied by making the use of chelating agents like EDTA, NTA etc.
2] Co-ordination complexes are having extensive analytical applications with techniques like titrimetry, spectrometry, polarography, chromatography and electrophoresis.

3] Co-ordination complexes are helpful for water-softening, inactivation of metal ions, precipitation analysis, catalytic reactions and a great variety of specific analytical tests both qualitative and quantitative.

4] Unnatural chelating agents are used in biological systems for (a) destructing of organisms by chelation of essential metals-bactericidal and fungicidal action, (b) inhibition of certain metals and metal enzymes for the purpose of studying functions of metals and enzymes in biological media and (c) removal of undesirable and harmful metals from living organisms.

**Importance of Pyrazoles, Isoxazoles, Pyrazolines and Isoxazolines :**

Different substituted pyrazoles, isoxazoles, pyrazolines and isoxazolines are known to have as anti-inflammatory agents, analgesic, anaesthetic, insecticidal, bactericidal and pharmaceutical, fungicides, antiviral, antifungal, antitubercular, miticides, pesticides, anticonvulsants, antidiabetic properties.

Many drugs and dyes contain the pyrazole nucleus. So this class of compounds have been widely studied and continues to attract even today much attention. Pyrazoles are known to have their physiological activities.\(^{57-63}\) Herbicidal compositions containing pyrazole derivatives like aryl amino pyrazoles have been prepared by Seki et al\(^ {64}\).

Isoxazoles are the five membered heterocyclic ring systems containing both oxygen and nitrogen atoms in 1,2 position. Isoxazole
derivatives have been reported to possess antitubercular\textsuperscript{65}, antiviral\textsuperscript{66} and antibacterial\textsuperscript{67} activities.

Pyrazolines are tested for bactericidal and fungicidal activity. Arrhenius\textsuperscript{68} reported substituted pyrazolines to be very effective in killing house flies on contact. Recently, some N-acetyl, N-aryl pyrazoline derivatives are reported as more effective than isoxazoles and other counterparts. Literature survey reveals the importance of pyrazolines as beaching agents and luminescent apart from their use as drugs. Pyrazolines and isoxazolines are widely applicable in photography due to their excellent sensitivity.

**General methods for studying the proton-ligand and metal-ligand stability constants:**

The proton-ligand and metal-ligand stability constants of the complexes can be determined by number of methods shown as,

1) pH-metry  
2) Spectrophotometry  
3) Optical activity  
4) Ion exchange measurements  
5) Polarography  
6) Gas chromatography

Our present work deals with the study of dissociation constants (proton-ligand stability constants) in 70\% dioxane-water mixture pH-metrically. Metal complex formation may be considered due to the displacement of a proton from the ligand causing a drop in the pH value of the solution. Irving and Rossotti\textsuperscript{69} have given a method for calculating the stability constants of proton-ligand and metal-ligand complexes by pH-metry. The general technique, that is followed due to Calvin and Bjerrum\textsuperscript{70}.

Literature survey reveals that a very few work on proton-ligand and metal-ligand stability constants with some substituted pyrazoles,
isoxazoles, pyrazolines and isoxazolines have been carried out hence in a view of the analytical applications and for the sake of curiosity, it is worthwhile to know the dissociation constant of phenolic –OH group and effect of substitutents on proton-ligand stability constants. Therefore, the present physico-chemical work is undertaken to make a systematic study for determining proton-ligand stability constants of some nitrosubstituted heterocycles pH-metrically at 0.1 M ionic strength in 70% dioxane-water mixture and 27±0.1°C temperature.
6.2 ORIGIN OF THE PROBLEM, PROBLEM AND SUMMARY OF THE WORK

ORIGIN OF THE PROBLEM

Historically coordination chemistry is of comparatively recent origin. Prussian blue, obtained by Diesbach Barin in 1704 may be considered as the earliest recorded co-ordination compound and its physical properties are studied by electrical devices such as pH-metry, potentiometry, spectrophotometry etc. The beginning of co-ordination chemistry is however, usually dated from the discovery of cobaltamines by Tassert in 1798 and properties of many azole compounds have been investigated using analytical pH-metry process. This technique has been extensively explained so far by J. Bjerrum\textsuperscript{71} and Irving-Rossotti\textsuperscript{72}. Azoles such as substituted pyrazoles and isoxazoles are essential pharmophore of number of a antibiotic activities. Isoxazoles and isoxazolines are known for their versatile physiological antibacterial, antiviral, antitubercular and antifungal activities.\textsuperscript{73-75}

pH-Metric technique is simple, elegant, rapid, most versatile, cheap and do not need any sophisticated instruments, which is very much used for investigating the physical properties such as proton-ligand and metal-ligand stability constants of organic drugs (pyrazolines, isoxazolines, pyrazoles and isoxazoles).

Ozawa et al\textsuperscript{76} tested and reported substituted isoxazoles and isoxazolines have bactericidal and fungicidal activity. He found that substituted isoxazoles and isoxazolines have been used as antimicrobial, insecticide, anticancer and antibiotic active materials. He also found that substituted isoxazolines are effective in killing house flies in contact. Jain
et al\textsuperscript{77} reported that, isoxazoles differ strongly from pyrazole in its remarkable stability and more basic nature. Recently, international efforts on isoxazoles and isoxazolines are made in agriculture Canada, Saskatoon and Indian agriculture research Institute.

Since last 45 years, considerable research work has been done on the study of complexes in solution\textsuperscript{1,2,78}. Coordination compound plays an important role in numerous chemical and biological systems like separation of lanthanides, water softening, ion exchange resins, electroplating, dyeing, antioxidants, photosynthesis in plants, removal of undesirable and harmful metals from living organism etc. Metal complexation not only brings the reaching molecules together to give activated complex\textsuperscript{79} but also polarise electrons from the ligands towards the metal. The relation between stability and basicity of the ligands is indicated by the formation constant and free energy change value. Bulkier group increases the basicity as well as stability of the ligands. The stability of the complexes is determined by the nature of the central metal atom and the ligands and depends on the same characterisation of the ligands as considered for the cation as complexes reacted with monoatomic ligands.

Theoretical study of some substituted pyrazoles and isoxazoles with rare earth metal complexes has been made by Kuznetsov et al\textsuperscript{80}. Parallel solution phase synthesis of N-substituted-2-pyrazole has been carried out by Udobaner et al\textsuperscript{81}.

Taking in consideration the applicability and remarkable properties of substituted pyrazoles, isoxazoles, pyrazolines and isoxazolines a systematic study of these compounds for determining the proton-ligand stability constants (pK) has been made pH-metrically at 0.1 M ionic strength.
PROBLEM

The present work deals with the study of physico-chemical properties such as proton-ligand stability constants of newly synthesised nitro substituted pyrazole, isoxazole, thioisoxazole, pyrazoline, isoxazoline and thioisoxazoline. It was thought interesting to study dissociation constants of newly synthesized compounds under suitable conditions and the presence of –OH group in these structures was confirmed at 0.1 M ionic strength. To study the dissociation constants and association constants in 70% dioxane-water mixture pH-metrically, the following compounds were used as chelating agents (ligands).

Ligands :

1. 1-H-3-(2"'-Hydroxy-3"'-nitro-5"'-methylphenyl)-5-phenyl-2-pyrazole [HNMPPP], (XIVa) (Ligand No. 1)
2. 3-(2"'-Hydroxy-3"'-nitro-5"'-methylphenyl)-5-phenyl isoxazole [HNMPPI] (XVIIIa) (Ligand No. 2)
3. 3-(2"'-Hydroxy-3"'-nitro-5"'-methylphenyl)-5-phenyl thioisoxazole [HNMPPTI] (XXa) (Ligand No. 3)
4. 1-H-3-(2"'-Hydroxy-3"'-nitro-5"'-methylphenyl)-5-(4'-methoxyphenyl)-Δ²-pyrazoline [HNMPMPP] (IVb) (Ligand No. 4)
5. 3-(2"'-Hydroxy-3"'-nitro-5"'-methylphenyl)-5-(4'-methoxyphenyl)-isoxazoline [HNMPMPI] (VIIIb) (Ligand No. 5)
6. 3-(2"'-Hydroxy-3"'-nitro-5"'-methylphenyl)-5-(4'-methoxyphenyl)-thioisoxazoline [HNMPMPTI] (Xb) (Ligand No. 6)

To understand the effect of substituting group in 70% dioxane-water mixture, the experimental data of proton-ligand stability constants (pK) values of ligands L₁ to L₆ are used.
SUMMARY OF THE WORK

The ligand No. [1] 1-H-3-(2"-Hydroxy-3"-nitro-5"-methyl-phenyl)-5-phenyl-2-pyrazole [HNMPPP], (XIVa), m.p. 210°C, [2] 3-(2"-Hydroxy-3"-nitro-5"-methylphenyl)-5-phenyl isoxazole [HNMPI], (XVIIIa), m.p. 141°C, [3] 3-(2"-Hydroxy-3"-nitro-5"-methylphenyl)-5-phenyl thioisoxazole [HNMPPTI], (XXa), m.p. 155°C, [4] 1-H-3-(2"-Hydroxy-3"-nitro-5"-methyl-phenyl)-5-(4'-methoxyphenyl)-Δ²-pyrazoline [HNMPMPP], (IVb), m.p. 189°C, [5] 3-(2"-Hydroxy-3"-nitro-5"-methylphenyl)-5-(4'-methoxyphenyl)-isoxazoline [HNMPMPI], (VIIIb), m.p. 215°C, [6] 3-(2"-Hydroxy-3"-nitro-5"-methyl-phenyl)-5-(4'-methoxyphenyl)-thioisoxazoline [HNMPMPTI], (Xb), m.p. 163°C were used. They are synthesized by standard methods as described in 3.3 (Chapter 1,2, 3 and 4) of this thesis. The structure of all these compounds are confirmed on the basis of chemical properties, elemental analysis and spectral data (IR, UV, PMR). The purity of compounds synthesised was checked by TLC on microscopic slides with silica gel 'G' layers. Calvin and Mechior's technique known as Calvin-Bjerrum titration has been employed in the present investigation and is used to understand dissociation of –OH group and proton-ligand stability constants.
6.3 EXPERIMENTAL AND DISCUSSION OF THE RESULTS

[A] REAGENTS :

1. Distilled Water -

   Distilled water used was free from carbondioxide and pH of this water was about 6.90.

2. Sodium Hydroxide -

   Sodium hydroxide pellets (AR) was used and its solution of 0.1 M was prepared in distilled water free from carbondioxide.

3. Perchloric Acid -

   Perchloric acid (AR) was used and its solution of 0.1 M was prepared in distilled water.

4. Sodium Perchlorate -

   Sodium perchlorate (AR) was used and its solution of 1 M was prepared in distilled water.

Chelating Agents :

1) Ligand solution of 0.01 M were prepared in 70% dioxane-water medium.

2) 0.1475 gm Ligand No. 1 was dissolved in 50 ml 70% dioxane : 0.01 M solution.

3) 0.148 gm Ligand No. 2 was dissolved in 50 ml 70% dioxane : 0.01 M solution.

4) 0.156 gm Ligand No. 3 was dissolved in 50 ml 70% dioxane : 0.01 M solution.
5) 0.1635 gm Ligand No. 4 was dissolved in 50 ml 70% dioxane : 0.01 M solution.

6) 0.164 gm Ligand No. 5 was dissolved in 50 ml 70% dioxane : 0.01 M solution.

7) 0.172 gm Ligand No. 6 was dissolved in 50 ml 70% dioxane : 0.01 M solution.

[B] INSTRUMENT:

Equip-Tronics pH-meter with model EQ 614 (accuracy ± 0.05 units) using combined glass electrode and saturated calomel electrode at 27°C ± 0.1°C was used for pH measurements. It was calibrated by buffer solution of pH 4.00, 7.00 and 9.2 at 27°C ± 0.1°C before processing the titrations. The practical values (B. values) are converted into real values of pH of solution by applying the correction proposed by Van-Uitert and Hass.83

[C] CALVIN-BJERRUM TITRATION:

The experimental procedure involved two types of pH-metric titration using Calvin-Bjerrum titration process.

1) Free acid (0.1 M) titration :- 5 ml HClO₄ (0.1 M) + 5 ml NaClO₄ (1 M) + 35 ml dioxane + 5 ml water (V° = 50 ml), and

2) Free acid (0.1 M) + Ligand (2x10⁻³ M) titration :- 5 ml HClO₄ (0.1 M) + 5 ml NaClO₄ (1 M) + 10 ml ligand + 25 ml dioxane + 5 ml water (V° = 50 ml), are titrated against standard alkali (NaOH) solution by bubbling nitrogen gas to avoid oxidation. The ionic strength of all the solutions was maintained constant (0.1 M) by adding an appropriate amount of 1 M NaClO₄ solution.
The titrations were carried out in 100 ml pyrex glass beaker in an ice cold water bath maintained at constant temperature (27 ± 0.1°C). Nitrogen gas was purged for chemically inert atmosphere. The readings were recorded for each addition of 0.2 ml/0.1ml.

Titrination curves for all the systems are constructed by plotting the graph between volume of NaOH and pH. The curve has been designated as below.

(i) Acid titration curve (A)
(ii) Acid + ligand titration curve (A+L)

**Methods for Determination of Proton-Ligand Stability Constants :**

The dissociation constant of substituted ligands L₁, L₂, L₃, L₄, L₅ and L₆ were determined at 0.1 M ionic strength pH-metrically. The reagents or ligands used in the present investigation are monobasic acid having only one dissociable H⁺ ion from −OH group. Hence ligand can be represented as HL.

\[ HL \rightleftharpoons H^+ + L^- \]

The titration curves of the acid and the ligand deviate at about pH 6.0 and it is then increased continuously upto pH 10.00. The deviation between acid curve from ligand for all the systems showed the dissociation of H⁺ ions from −OH groups of the ligands (Table 1 to 6).

**Proton-Ligand Formation Number (nA) :**

Proton-ligand formation numbers (nA) were calculated by applying Irving and Rossotti expression.
\( n_A = \gamma - \frac{(E^0 + N) \Delta V}{(V^0 + V_1) (T_L^0)} \)

where,

\( \gamma = \) Number of dissociable proton from ligand.

\( V^0 = \) Initial volume of the solution (50 ml)

\( N = \) Normality of NaOH solution (0.1 M)

\( T_L^0 = \) Concentrations of ligand in 50 ml solution (2x10^{-3} M)

\( E^0 = \) Initial concentration of free acid (HClO\(_4\)) solution (0.01 M)

\( V_1 = \) Volume of free acid with respect to pH of the solution.

\( (V_2 - V_1) = \Delta V = \) Volume of alkali consumed by acid and ligand on the same pH.

The values of \( n_A \) along with the difference between the volume of alkali required for acid and ligand titration curve (\( V_2 - V_1 \)) are presented in Table Nos. 7 to 12.

It could be seen from Table No. 7 to 12 that the values of \( n_A \) decrease with increase in pH of the solution due to replacement of H\(^+\) ions from −OH groups.

The titration curves of the acid and the ligand deviated at above pH 6.0 and then it is raised upto pH 10.00. The deviation between acid curves from ligand curves for all the systems showed the dissociation of H\(^+\) ions from −OH groups (Fig. No. 1 to 6).

**PROTON-LIGAND FORMATION CURVES**:

The formation curves were constructed by plotting the values of \( n_A \) against pH of solution (Fig. 7 to 12). The proton-ligand stability constants (pK values) were calculated from formation curves. The value of pH at which
$n_A = 0.5$ corresponds to the pK value, this is called half integral method and accurate pK values are calculated by pointwise calculation method which are presented in Table No. 13.

The pK values of substituted sulphonic acids were determined using similar procedure (half integral method) by Jahagirdar et al$^{84}$ and Mahajan et al$^{85}$.

**DISCUSSION:**

It would be seen from Table No. 13 that, in ligand systems $L_1$ to $L_6$ there is a steric hindrance due to electron releasing $-\text{CH}_3$ group and electron withdrawing $-\text{NO}_2$ group. There is no such an appreciable change in proton-ligand stability constant (pK) because steric hindrance effect is compensated due to electron withdrawing effect of $-\text{NO}_2$ group and electron releasing effect of $-\text{CH}_3$ group. There is reduction in pK values of the ligands $L_4$, $L_5$ and $L_6$ as compared to the pK values of ligand $L_1$, $L_2$ and $L_3$. This may be due to the fact of the presence of $-\text{OCH}_3$ as a electron withdrawing group in ligand $L_4$, $L_5$ and $L_6$ and involving double bond of electron density in five membered ring of ligand $L_1$, $L_2$ and $L_3$.

**CONCLUSION:**

It is observed from the titration curves between (acid + ligand) for all the systems that the deviation between the curves is found at about pH 6.0 and it is then increased continuously upto pH 10.00. This may due to the dissociation of phenolic -OH group present in the ligand and also indicates the commencement of complex formation from this pH (pH = 6.0). During the titration process, solution colour changed from light brown to dark brown. This also shows the formation of complex between acid and ligand.
It could be seen from Table No. 13 that, the order of pK values of the ligands is found to be as,

\[ \text{pK} \text{ Ligand 1} > \text{pK} \text{ Ligand 4} \]
\[ \text{pK} \text{ Ligand 2} > \text{pK} \text{ Ligand 5} \]
\[ \text{pK} \text{ Ligand 3} > \text{pK} \text{ Ligand 6} \]

This may be due to the fact of the presence of \(-\text{OCH}_3\) as a electron withdrawing group in Ligand 4, Ligand 5 and Ligand 6. The electron withdrawing \(-\text{OCH}_3\) group reduces the pK values of these ligands and involving double bond of electron density in five membered ring of Ligand 1, Ligand 2 and Ligand 3. The presence of double bond electron density in the five membered ring increases the pK values of these ligands.
Table 1: pH-metric Titration Data
System – Ligand No. 1 [HNMPPP]

Medium – 70% Dioxane-water
E$^0$ = 1.00 x 10^{-2} M
T_L$^0$ = 2.00 x 10^{-3} M
μ = 0.1 M

Temp. = 27 ± 0.1°C
V$^0$ = 50 ml
N = 0.1 M

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Volume of NaOH (ml)</th>
<th>Free Acid Titration (A) pH</th>
<th>Free Acid + Ligand Titration (A+L) pH</th>
</tr>
</thead>
<tbody>
<tr>
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Table 2: pH-metric Titration Data
System – Ligand No. 2 [HNMPPI]

Medium – 70% Dioxane-water
E<sup>0</sup> = 1.00 x 10<sup>-2</sup> M  T<sub>L</sub><sup>0</sup> = 2.00 x 10<sup>-3</sup> M
μ = 0.1 M  V<sup>0</sup> = 50 ml
Temp. = 27 ± 0.1°C  N = 0.1 M

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Table 3: pH-metric Titration Data

System – Ligand No. 3 [HNMPPTI]

Medium – 70% Dioxane-water

E0 = 1.00 x 10^{-2} M
T_L0 = 2.00 x 10^{-3} M
μ = 0.1 M
Temp. = 27 ± 0.1°C
V_0 = 50 ml
N = 0.1 M

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Table 4: pH-metric Titration Data  
System – Ligand No. 4 [HNPMPP]

Medium – 70% Dioxane-water  
E\textsuperscript{0} = 1.00 \times 10^{-2} \text{ M}  
T_{L}^{0} = 2.00 \times 10^{-3} \text{ M}  
\mu = 0.1 \text{ M}  
Temp. = 27 \pm 0.1^\circ \text{C}  
V^{0} = 50 \text{ ml}  
N = 0.1 \text{ M}

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Table 5: pH-metric Titration Data  
System – Ligand No. 5 [HNMPMPI]

Medium – 70% Dioxane-water  
E⁰ = 1.00 x 10⁻² M  
Tₗ⁰ = 2.00 x 10⁻³ M  
µ = 0.1 M  
Temp. = 27 ± 0.1°C  
V⁰ = 50 ml  
N = 0.1 M

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Table 6: pH-metric Titration Data
System – Ligand No. 6 [HNMPMPTI]

Medium – 70% Dioxane-water
E° = 1.00 x 10^-2 M \( T_{L}^{0} = 2.00 \times 10^{-3} \) M
\( \mu = 0.1 \) M

Temp. = 27 ± 0.1°C
\( V^{0} = 50 \) ml
\( N = 0.1 \) M

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Table 7: Determination of $\bar{n}_A$ Values

System – Ligand No. 1 [HNMPPP]

Medium – 70% Dioxane-water
Temp. = 27 ± 0.1°C

$E^0 = 1.00 \times 10^{-2}$ M
$T_L^0 = 2.00 \times 10^{-3}$ M
$V^0 = 50$ ml
$\mu = 0.1$ M
$N = 0.1$ M

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<th>Sr. No.</th>
<th>pH</th>
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<th>$V_2$ (ml)</th>
<th>$\Delta V = V_2 - V_1$ (ml)</th>
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Table 8: Determination of $\overline{n_A}$ Values

System – Ligand No. 2 [HNMPPI]

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Medium – 70% Dioxane-water  
$E^0 = 1.00 \times 10^{-2}$ M  
$T_L^0 = 2.00 \times 10^{-3}$ M  
$\mu = 0.1$ M  
Temp. = 27 ± 0.1°C  
$V^0 = 50$ ml  
$N = 0.1$ M
Table 9 : Determination of $\bar{n}_A$ Values

System – Ligand No. 3 [HNMPPTI]

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<td>3.30</td>
<td>0.75</td>
<td>0.2150</td>
</tr>
<tr>
<td>13.</td>
<td>9.20</td>
<td>2.60</td>
<td>3.40</td>
<td>0.80</td>
<td>0.1635</td>
</tr>
</tbody>
</table>
Table 10: Determination of $n_A$ Values

System – Ligand No. 4 [HNMPMPP]

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>pH</th>
<th>$V_1$ (ml)</th>
<th>$V_2$ (ml)</th>
<th>$\Delta V = V_2 - V_1$ (ml)</th>
<th>$\bar{n}_A$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.00</td>
<td>2.05</td>
<td>2.10</td>
<td>0.05</td>
<td>0.9472</td>
</tr>
<tr>
<td>2</td>
<td>5.50</td>
<td>2.07</td>
<td>2.17</td>
<td>0.10</td>
<td>0.8943</td>
</tr>
<tr>
<td>3</td>
<td>6.00</td>
<td>2.10</td>
<td>2.22</td>
<td>0.12</td>
<td>0.8733</td>
</tr>
<tr>
<td>4</td>
<td>6.50</td>
<td>2.10</td>
<td>2.25</td>
<td>0.15</td>
<td>0.8417</td>
</tr>
<tr>
<td>5</td>
<td>7.00</td>
<td>2.20</td>
<td>2.40</td>
<td>0.20</td>
<td>0.7893</td>
</tr>
<tr>
<td>6</td>
<td>7.50</td>
<td>2.35</td>
<td>2.60</td>
<td>0.25</td>
<td>0.7373</td>
</tr>
<tr>
<td>7</td>
<td>8.00</td>
<td>2.45</td>
<td>2.75</td>
<td>0.30</td>
<td>0.6854</td>
</tr>
<tr>
<td>8</td>
<td>8.20</td>
<td>2.45</td>
<td>2.85</td>
<td>0.40</td>
<td>0.5806</td>
</tr>
<tr>
<td>9</td>
<td>8.40</td>
<td>2.45</td>
<td>2.90</td>
<td>0.45</td>
<td>0.5234</td>
</tr>
<tr>
<td>10</td>
<td>8.60</td>
<td>2.50</td>
<td>3.05</td>
<td>0.55</td>
<td>0.4191</td>
</tr>
<tr>
<td>11</td>
<td>8.80</td>
<td>2.55</td>
<td>3.15</td>
<td>0.60</td>
<td>0.3721</td>
</tr>
<tr>
<td>12</td>
<td>9.00</td>
<td>2.55</td>
<td>3.25</td>
<td>0.70</td>
<td>0.2674</td>
</tr>
</tbody>
</table>
Table 11 : Determination of $\bar{n}_A$ Values

System – Ligand No. 5 [HNMPMPI]

Medium – 70% Dioxane-water

$E^0 = 1.00 \times 10^{-2}$ M \hspace{1cm} $T_L^0 = 2.00 \times 10^{-3}$ M

$\mu = 0.1$ M

$N = 0.1$ M

Temp. = 27 ± 0.1°C

$V^0 = 50$ ml

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>pH</th>
<th>$V_1$ (ml)</th>
<th>$V_2$ (ml)</th>
<th>$\Delta V = V_2 - V_1$ (ml)</th>
<th>$\bar{n}_A$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>6.20</td>
<td>2.05</td>
<td>2.10</td>
<td>0.05</td>
<td>0.9471</td>
</tr>
<tr>
<td>2.</td>
<td>6.50</td>
<td>2.10</td>
<td>2.16</td>
<td>0.06</td>
<td>0.9366</td>
</tr>
<tr>
<td>3.</td>
<td>7.00</td>
<td>2.20</td>
<td>2.30</td>
<td>0.10</td>
<td>0.8946</td>
</tr>
<tr>
<td>4.</td>
<td>7.50</td>
<td>2.40</td>
<td>2.55</td>
<td>0.15</td>
<td>0.8425</td>
</tr>
<tr>
<td>5.</td>
<td>8.00</td>
<td>2.40</td>
<td>2.65</td>
<td>0.25</td>
<td>0.7375</td>
</tr>
<tr>
<td>6.</td>
<td>8.20</td>
<td>2.45</td>
<td>2.80</td>
<td>0.35</td>
<td>0.6329</td>
</tr>
<tr>
<td>7.</td>
<td>8.40</td>
<td>2.45</td>
<td>2.90</td>
<td>0.45</td>
<td>0.5281</td>
</tr>
<tr>
<td>8.</td>
<td>8.60</td>
<td>2.50</td>
<td>3.00</td>
<td>0.50</td>
<td>0.4761</td>
</tr>
<tr>
<td>9.</td>
<td>8.80</td>
<td>2.55</td>
<td>3.20</td>
<td>0.65</td>
<td>0.3196</td>
</tr>
<tr>
<td>10.</td>
<td>9.00</td>
<td>2.60</td>
<td>3.30</td>
<td>0.70</td>
<td>0.2680</td>
</tr>
<tr>
<td>11.</td>
<td>9.20</td>
<td>2.65</td>
<td>3.40</td>
<td>0.075</td>
<td>0.2165</td>
</tr>
</tbody>
</table>
Table 12: Determination of $\bar{n}_A$ Values

System – Ligand No. 6 [HNMPMPTI]

Medium – 70% Dioxane-water
$E^0 = 1.00 \times 10^{-2}$ M
$T_L^0 = 2.00 \times 10^{-3}$ M
$\mu = 0.1$ M
$V^0 = 50$ ml
$N = 0.1$ M

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>pH</th>
<th>$V_1$ (ml)</th>
<th>$V_2$ (ml)</th>
<th>$\Delta V = V_2 - V_1$ (ml)</th>
<th>$\bar{n}_A$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>6.50</td>
<td>2.20</td>
<td>2.30</td>
<td>0.10</td>
<td>0.8946</td>
</tr>
<tr>
<td>2.</td>
<td>7.00</td>
<td>2.25</td>
<td>2.40</td>
<td>0.15</td>
<td>0.8421</td>
</tr>
<tr>
<td>3.</td>
<td>7.50</td>
<td>2.35</td>
<td>2.55</td>
<td>0.20</td>
<td>0.7798</td>
</tr>
<tr>
<td>4.</td>
<td>8.00</td>
<td>2.40</td>
<td>2.70</td>
<td>0.30</td>
<td>0.6851</td>
</tr>
<tr>
<td>5.</td>
<td>8.20</td>
<td>2.45</td>
<td>2.80</td>
<td>0.35</td>
<td>0.6333</td>
</tr>
<tr>
<td>6.</td>
<td>8.40</td>
<td>2.50</td>
<td>3.00</td>
<td>0.50</td>
<td>0.4761</td>
</tr>
<tr>
<td>7.</td>
<td>8.60</td>
<td>2.50</td>
<td>3.10</td>
<td>0.60</td>
<td>0.3714</td>
</tr>
<tr>
<td>8.</td>
<td>8.80</td>
<td>2.50</td>
<td>3.20</td>
<td>0.70</td>
<td>0.2666</td>
</tr>
<tr>
<td>9.</td>
<td>9.00</td>
<td>2.55</td>
<td>3.30</td>
<td>0.75</td>
<td>0.2150</td>
</tr>
<tr>
<td>10.</td>
<td>9.20</td>
<td>2.60</td>
<td>3.45</td>
<td>0.85</td>
<td>0.1112</td>
</tr>
</tbody>
</table>

Table 13: pK Values of Ligands

Proton-Ligand Stability Constants (pK)

<table>
<thead>
<tr>
<th>Sr No.</th>
<th>System</th>
<th>Half integral Value (PK)</th>
<th>Point Wise Value of Calculation (PK)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Ligand No. 1</td>
<td>8.52</td>
<td>8.50 ± 0.03</td>
</tr>
<tr>
<td>2.</td>
<td>Ligand No. 2</td>
<td>8.67</td>
<td>8.69 ± 0.04</td>
</tr>
<tr>
<td>3.</td>
<td>Ligand No. 3</td>
<td>8.40</td>
<td>8.39 ± 0.03</td>
</tr>
<tr>
<td>4.</td>
<td>Ligand No. 4</td>
<td>8.41</td>
<td>8.43 ± 0.04</td>
</tr>
<tr>
<td>5.</td>
<td>Ligand No. 5</td>
<td>8.49</td>
<td>8.48 ± 0.02</td>
</tr>
<tr>
<td>6.</td>
<td>Ligand No. 6</td>
<td>8.22</td>
<td>8.19 ± 0.04</td>
</tr>
</tbody>
</table>
### Table 14: Standard Deviation (\(\sigma\)) of Ligand No. 3

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>PH</th>
<th>Conc. of NaOH 0.1M (n_A) (Expt)</th>
<th>Conc. of NaOH 0.13 M (n_A) (Calcu)</th>
<th>(\Delta n_A)</th>
<th>((\Delta n_A)^2)</th>
<th>(\sigma = \left( \frac{\sum(\Delta n_A)^2}{n - 1} \right)^{\frac{1}{2}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.50</td>
<td>0.8946</td>
<td>0.8900</td>
<td>+4.6x10^{-3}</td>
<td>21.16x10^{-6}</td>
<td>0.00413</td>
</tr>
<tr>
<td>2</td>
<td>7.00</td>
<td>0.8421</td>
<td>0.8451</td>
<td>-3.0x10^{-3}</td>
<td>9.00x10^{-6}</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>7.20</td>
<td>0.7368</td>
<td>0.7293</td>
<td>+7.5x10^{-3}</td>
<td>56.25x10^{-6}</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>7.40</td>
<td>0.6845</td>
<td>0.6862</td>
<td>+1.7x10^{-3}</td>
<td>2.89x10^{-6}</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>7.60</td>
<td>0.6319</td>
<td>0.6330</td>
<td>+2.1x10^{-3}</td>
<td>4.41x10^{-6}</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>7.80</td>
<td>0.5793</td>
<td>0.5821</td>
<td>-2.8x10^{-3}</td>
<td>7.84x10^{-6}</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>8.00</td>
<td>0.5276</td>
<td>0.5300</td>
<td>-2.4x10^{-3}</td>
<td>5.76x10^{-6}</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>8.20</td>
<td>0.4727</td>
<td>0.4782</td>
<td>-5.5x10^{-3}</td>
<td>30.25x10^{-6}</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>8.40</td>
<td>0.4238</td>
<td>0.4260</td>
<td>-2.2x10^{-3}</td>
<td>4.84x10^{-6}</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>8.60</td>
<td>0.3741</td>
<td>0.3731</td>
<td>+1.0x10^{-3}</td>
<td>1.00x10^{-6}</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>8.80</td>
<td>0.2666</td>
<td>0.2600</td>
<td>+6.6x10^{-3}</td>
<td>43.56x10^{-6}</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>9.00</td>
<td>0.2150</td>
<td>0.2160</td>
<td>1.0x10^{-3}</td>
<td>1.00x10^{-6}</td>
<td></td>
</tr>
</tbody>
</table>

Standard deviation is evaluated by keeping all the conditions constant except the concentration of alkali NaOH for all the systems. Representative value of standard deviation of ligand No. 3 is presented in above Table No. 14. The value of standard deviation (\(\sigma = 0.00413\)) clearly showed that the values of \(n_A\) evaluated are found to be correct.
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### List of Newly Synthesised Heterocycles

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Compd. No.</th>
<th>Name of the compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>IIa</td>
<td>1-(2&quot;-Hydroxy-3&quot;-nitro-5&quot;-methylphenyl)-3-phenyl-2-propen-1-one</td>
</tr>
<tr>
<td>2.</td>
<td>IIb</td>
<td>1-(2&quot;-Hydroxy-3&quot;-nitro-5&quot;-methylphenyl)-3-(4'-methoxyphenyl)-2-propen-1-one</td>
</tr>
<tr>
<td>3.</td>
<td>IIc</td>
<td>1-(2&quot;-Hydroxy-3&quot;-nitro-5&quot;-methylphenyl)-3-(3'-nitrophenyl)-2-propen-1-one</td>
</tr>
<tr>
<td>4.</td>
<td>IIId</td>
<td>1-(2&quot;-Hydroxy-3&quot;-nitro-5&quot;-methylphenyl)-3-(3',4'-methylene dioxyphenyl)-2-propen-1-one</td>
</tr>
<tr>
<td>5.</td>
<td>IIIa</td>
<td>2-Phenyl-6-methyl-8-nitroflavanone</td>
</tr>
<tr>
<td>6.</td>
<td>IIIb</td>
<td>2-(4'-Methoxyphenyl)-6-methyl-8-nitroflavanone</td>
</tr>
<tr>
<td>7.</td>
<td>IIIc</td>
<td>2-(3'-Nitrophenyl)-6-methyl-8-nitroflavanone</td>
</tr>
<tr>
<td>8.</td>
<td>IIIId</td>
<td>2-(3',4'-Methylene dioxyphenyl)-6-methyl-8-nitroflavanone</td>
</tr>
<tr>
<td>9.</td>
<td>IVa</td>
<td>1-H-3-(2&quot;-Hydroxy-3&quot;-nitro-5&quot;-methylphenyl)-5-phenyl-Δ²-pyrazoline</td>
</tr>
<tr>
<td>10.</td>
<td>IVb</td>
<td>1-H-3-(2&quot;-Hydroxy-3&quot;-nitro-5&quot;-methylphenyl)-5-(4'-methoxyphenyl)-Δ²-pyrazoline</td>
</tr>
<tr>
<td>11.</td>
<td>IVc</td>
<td>1-H-3-(2&quot;-Hydroxy-3&quot;-nitro-5&quot;-methylphenyl)-5-(3'-nitrophenyl)-Δ²-pyrazoline</td>
</tr>
<tr>
<td>12.</td>
<td>IVd</td>
<td>1-H-3-(2&quot;-Hydroxy-3&quot;-nitro-5&quot;-methylphenyl)-5-(3',4'-methylene dioxyphenyl)-Δ²-pyrazoline</td>
</tr>
<tr>
<td>13.</td>
<td>Va</td>
<td>1-Acetyl-3-(2&quot;-hydroxy-3&quot;-nitro-5&quot;-methylphenyl)-5-phenyl-Δ²-pyrazoline</td>
</tr>
<tr>
<td>14.</td>
<td>Vb</td>
<td>1-Acetyl-3-(2&quot;-hydroxy-3&quot;-nitro-5&quot;-methylphenyl)-5-(4'-methoxyphenyl)-Δ²-pyrazoline</td>
</tr>
<tr>
<td>15.</td>
<td>Vc</td>
<td>1-Acetyl-3-(2&quot;-hydroxy-3&quot;-nitro-5&quot;-methylphenyl)-5-(3'-nitrophenyl)-Δ²-pyrazoline</td>
</tr>
<tr>
<td>16.</td>
<td>Vd</td>
<td>1-Acetyl-3-(2&quot;-hydroxy-3&quot;-nitro-5&quot;-methylphenyl)-5-(3',4'-methylene dioxyphenyl)-Δ²-pyrazoline</td>
</tr>
<tr>
<td>17.</td>
<td>VIa</td>
<td>1-Acetyl-3-(2&quot;-acetoxy-3&quot;-nitro-5&quot;-methylphenyl)-5-phenyl-Δ²-pyrazoline</td>
</tr>
<tr>
<td>18.</td>
<td>VIb</td>
<td>1-Acetyl-3-(2&quot;-acetoxy-3&quot;-nitro-5&quot;-methylphenyl)-5-(4'-methoxyphenyl)-Δ²-pyrazoline</td>
</tr>
<tr>
<td>19.</td>
<td>VIc</td>
<td>1-Acetyl-3-(2&quot;-acetoxy-3&quot;-nitro-5&quot;-methylphenyl)-5-(3'-nitrophenyl)-Δ²-pyrazoline</td>
</tr>
</tbody>
</table>
20. VIId 1-Acetyl-3-(2''-acetoxy-3''-nitro-5''-methylphenyl)-5-(3',4'-methylene dioxyphenyl)-2-pyrazoline
21. VIIa 1-Benzoyl-3-(2''-hydroxy-3''-nitro-5''-methylphenyl)-5-phenyl-Δ²-pyrazoline
22. VIIb 1-Benzoyl-3-(2''-hydroxy-3''-nitro-5''-methylphenyl)-5-(4'-methoxyphenyl)-Δ²-pyrazoline
23. VIIc 1-Benzoyl-3-(2''-hydroxy-3''-nitro-5''-methylphenyl)-5-(3'-nitrophenyl)-Δ²-pyrazoline
24. VIId 1-Benzoyl-3-(2''-hydroxy-3''-nitro-5''-methylphenyl)-5-(3',4'-methylene dioxyphenyl)-Δ²-pyrazoline
25. VIIIa 3-(2''-Hydroxy-3''-nitro-5''-methylphenyl)-5-phenyl-isoxazoline
26. VIIIb 3-(2''-Hydroxy-3''-nitro-5''-methylphenyl)-5-(4'-methoxyphenyl)-isoxazoline
27. VIIIc 3-(2''-Hydroxy-3''-nitro-5''-methylphenyl)-5-(3'-nitrophenyl)-isoxazoline
28. VIIId 3-(2''-Hydroxy-3''-nitro-5''-methylphenyl)-5-(3',4'-methoxyphenyl)-isoxazoline
29. IXa 3-(2''-Acetoxy-3''-nitro-5''-methylphenyl)-5-phenyl-thioisoxazoline
30. IXb 3-(2''-Acetoxy-3''-nitro-5''-methylphenyl)-5-(4'-methoxyphenyl)-thioisoxazoline
31. IXc 3-(2''-Acetoxy-3''-nitro-5''-methylphenyl)-5-(3'-nitrophenyl)-thioisoxazoline
32. IXd 3-(2''-Acetoxy-3''-nitro-5''-methylphenyl)-5-(3',4'-methoxyphenyl)-thioisoxazoline
33. Xa 3-(2''-Hydroxy-3''-nitro-5''-methylphenyl)-5-phenyl-thioisoxazoline
34. Xb 3-(2''-Hydroxy-3''-nitro-5''-methylphenyl)-5-(4'-methoxyphenyl)-thioisoxazoline
35. Xc 3-(2''-Hydroxy-3''-nitro-5''-methylphenyl)-5-(3'-nitrophenyl)-thioisoxazoline
36. Xd 3-(2''-Hydroxy-3''-nitro-5''-methylphenyl)-5-(3',4'-methylene dioxyphenyl)-thioisoxazoline
37. XLa 3-(2''-Acetoxy-3''-nitro-5''-methylphenyl)-5-phenyl-thioisoxazoline
38. XGb 3-(2''-Acetoxy-3''-nitro-5''-methylphenyl)-5-(4'-methoxyphenyl)-thioisoxazoline
39. XIc 3-(2''-Acetoxy-3''-nitro-5''-methylphenyl)-5-(3'-nitrophenyl)-thioisoxazoline
40. XId 3-(2''-Acetoxy-3''-nitro-5''-methylphenyl)-5-(3',4'-methylene dioxyphenyl)-thioisoxazoline
41. XIIa 2-Phenyl-6-methyl-8-nitroflavone
42. XIIb 2-(4'-Methoxyphenyl)-6-methyl-8-nitroflavone
43. XIIc 2-(3'-Nitrophenyl)-6-methyl-8-nitroflavone
44. XIIId 2-(3',4'-Methylene dioxyphenyl)-6-methyl-8-nitroflavone
45. XIIIa 1-(2'-Hydroxy-3''-nitro-5''-methylphenyl)-3-phenyl-2,3-dibromopropan-1-one
46. XIIIb 1-(2'-Hydroxy-3''-nitro-5''-methylphenyl)-3-(4'-methoxyphenyl)-2,3-dibromopropan-1-one
47. XIIIc 1-(2'-Hydroxy-3''-nitro-5''-methylphenyl)-3-(3'-nitrophenyl)-2,3-dibromopropan-1-one
48. XIIIId 1-(2'-Hydroxy-3''-nitro-5''-methylphenyl)-3-(3',4'-methylene dioxyphenyl)-2,3-dibromopropan-1-one
49. XIVa 1-H-3-(2''-Hydroxy-3''-nitro-5''-methylphenyl)-5-phenyl-2-pyrazole
50. XIVb 1-H-3-(2''-Hydroxy-3''-nitro-5''-methylphenyl)-5-(4'-methoxyphenyl)-2-pyrazole
51. XIVc 1-H-3-(2''-Hydroxy-3''-nitro-5''-methylphenyl)-5-(3'-nitrophenyl)-2-pyrazole
52. XIVd 1-H-3-(2''-Hydroxy-3''-nitro-5''-methylphenyl)-5-(3',4'-methylene dioxyphenyl)-2-pyrazole
53. XVa 1-Acetyl-3-(2''-hydroxy-3''-nitro-5''-methylphenyl)-5-phenyl-2-pyrazole
54. XVb 1-Acetyl-3-(2''-hydroxy-3''-nitro-5''-methylphenyl)-5-(4'-methoxyphenyl)-2-pyrazole
55. XVc 1-Acetyl-3-(2''-hydroxy-3''-nitro-5''-methylphenyl)-5-(3'-nitrophenyl)-2-pyrazole
56. XVD 1-Acetyl-3-(2''-hydroxy-3''-nitro-5''-methylphenyl)-5-(3',4'-methylene dioxyphenyl)-2-pyrazole
57. XVIA 1-Acetyl-3-(2''-acetoxy-3''-nitro-5''-methylphenyl)-5-phenyl-2-pyrazole
58. XVIB 1-Acetyl-3-(2''-acetoxy-3''-nitro-5''-methylphenyl)-5-(4'-methoxyphenyl)-2-pyrazole
59. XVIC 1-Acetyl-3-(2''-acetoxy-3''-nitro-5''-methylphenyl)-5-(3'-nitrophenyl)-2-pyrazole
60. XVID 1-Acetyl-3-(2''-acetoxy-3''-nitro-5''-methylphenyl)-5-(3',4'-methylene dioxyphenyl)-2-pyrazole
61. XVIIA 1-Benzoyl-3-(2''-hydroxy-3''-nitro-5''-methylphenyl)-5-phenyl-2-pyrazole
62. XVIIIB 1-Benzoyl-3-(2''-hydroxy-3''-nitro-5''-methylphenyl)-5-(4'-methoxyphenyl)-2-pyrazole
63. XVIIc  1-Benzoyl-3-(2"-hydroxy-3"-nitro-5"-methylphenyl) -
5-(3'-nitrophenyl)-2-pyrazole
64. XVIIId  1-Benzoyl-3-(2"-hydroxy-3"-nitro-5"-methylphenyl) -
5-(3',4'-methylene dioxyphenyl)-2-pyrazole
65. XVIIIa  3-(2"-Hydroxy-3"-nitro-5"-methylphenyl)-5-phenyl-
isoaxazole
66. XVIIIb  3-(2"-Hydroxy-3"-nitro-5"-methylphenyl)-5-(4'-methoxy-
phenyl)-isoaxazole
67. XVIIIc  3-(2"-Hydroxy-3"-nitro-5"-methylphenyl)-5-(3'-nitro-
phenyl)-isoaxazole
68. XVIIIId  3-(2"-Hydroxy-3"-nitro-5"-methylphenyl)-5-
(3',4'-methylene dioxyphenyl)-isoaxazole
69. XIXa  3-(2"-Acetoxy-3"-nitro-5"-methylphenyl)-5-phenyl-
isoaxazole
70. XIXb  3-(2"-Acetoxy-3"-nitro-5"-methylphenyl)-5-(4'-methoxy-
phenyl)-isoaxazole
71. XIXc  3-(2"-Acetoxy-3"-nitro-5"-methylphenyl)-5-(3'-nitro-
phenyl)-isoaxazole
72. XIXd  3-(2"-Acetoxy-3"-nitro-5"-methylphenyl)-5-
(3',4'-methylene dioxyphenyl)-isoaxazole
73. XXa  3-(2"-Hydroxy-3"-nitro-5"-methylphenyl)-5-phenyl-
thioisoxazole
74. XXb  3-(2"-Hydroxy-3"-nitro-5"-methylphenyl)-5-(4'-methoxy-
phenyl)-thioisoxazole
75. XXc  3-(2"-Hydroxy-3"-nitro-5"-methylphenyl)-5-(3'-nitro-
phenyl)-thioisoxazole
76. XXd  3-(2"-Hydroxy-3"-nitro-5"-methylphenyl)-5-
(3',4'-methylene dioxyphenyl)-thioisoxazole
77. XXIa  3-(2"-Acetoxy-3"-nitro-5"-methylphenyl)-5-phenyl-
thioisoxazole
78. XXIb  3-(2"-Acetoxy-3"-nitro-5"-methylphenyl)-5-(4'-methoxy-
phenyl)-thioisoxazole
79. XXIc  3-(2"-Acetoxy-3"-nitro-5"-methylphenyl)-5-(3'-nitro-
phenyl)-thioisoxazole
80. XXId  3-(2"-Acetoxy-3"-nitro-5"-methylphenyl)-5-
(3',4'-methylene dioxyphenyl)-thioisoxazole
List of Presentations


4) Research paper entitled "Synthesis of 3,5-diaryl isoxazolines and thioisoxazolines" presented in the National Conference on "Current Research Trends and Developments in Heterocyclic Chemistry", sponsored by UGC, New Delhi and organised by the Department of Chemistry, Post Graduate College of Science, Saifabad, Osmania University, Hyderabad-500004, India held on 17th and 18th March 2006.

5) Research paper entitled "Studies on proton-ligand stability constants of some Nitrosubstituted Heterocycles pH-metrically at 0.1M ionic strength" presented in the "Forty third Annual convention of chemists 2006", organised by the Indian Chemical Society, Kolkata-700009, India and hosted by the Department of Chemistry, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad-431004, India held on 23rd to 27th December 2006.

6) Research paper entitled "Synthesis and characterisation of some new Nitrosubstituted 3,5-diaryl isoxazoles, thioisoxazoles and corresponding heterocycles" presented in a poster session in the International conference on "Advances in drug discovery research", jointly organised by the Indian Society of Chemists and Biologist (ISCB), CDRL, Lucknow, India and Dr. Babasaheb Ambedkar Marathwada University, Aurangabad-431004, India held on 24th to 26th February 2006.
List of Publications


